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VISIBLE ABSORPTION SPECTRA OF SODIUM IN SODIUM IODIDE

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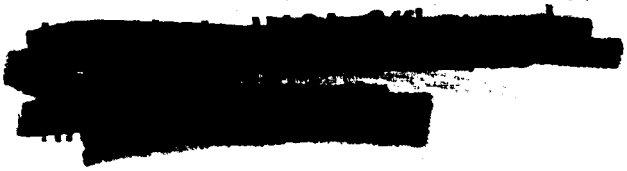
In order to establish a possible correlation between the visible absorption of alkali metals in molten alkali halides and F-center formation as observed in the solid, the visible absorption spectra of sodium in molten sodium iodide were obtained.

The experimental methods used in preparing the metal-salt mixture have already been described.[1,2] The methods involved the treatment of the metal-salt system with liquid ammonia. An excess of metal was introduced into the salt in order that a saturated solution be formed upon melting. In this way, a good approximation of the metal concentration could be made. A quartz cuvette 1 cm. in diameter was used. This container was wound with Nichrome ribbon and heated by means of a Variac. The steady-state temperatures were controlled to within $\pm 5^{\circ}$ C. The temperature was recorded by means of a platinum - platinum 13% rhodium thermocouple.

The data were recorded on a Beckman DK. In order to balance the instrument, the reference beam was attenuated. The results shown herein are therefore reported as relative percent transmission.

(1) I. Warshawsky and J. Greenberg, J. Inorg. and Nucl. Chem. (In Press).

(2) J. Greenberg and I. Warshawsky, J. Phys. Chem. (In Press).



RESULTS

The visible absorption spectra of a saturated solution of Na in Na in NaI at 675° C are shown in Fig. 1. The fact that the solution was saturated was verified by the presence of excess sodium at the bottom of the cuvette. As the temperature was increased to 700° C., the solution became completely opaque and no peak structure was observed. No discoloration of the glass was observed at the glass-liquid interface; however, in the space above the liquid the glass was discolored to a dark brown presumably due to sodium-metal attack.

DISCUSSION

The location of the F-center band in crystalline NaI has been reported to be at both 6090 Å and 588A Å.[3] Since increasing temperatures cause the peak of the F band to shift to lower energies,[4] the theoretical position of an F band in molten NaI would be at longer wavelengths. The presence of a band with a peak approximately 570 mμ for a saturated solution of Na in NaI at 675° C. does not therefore appear to be a function of F-center formation. Sodium atoms and molecules, however, do absorb in the region of the observed band. Since the position of the peak is close to that of the observed transitions for sodium atoms, it is likely that the primary absorbing species are sodium atoms. The absorption at shorter

(3) H. F. Ivey, Phys. Rev. 72, 341 (1947).

(4) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, London, 1948, p. 116.

wavelengths may be due to sodium molecules.[5] The presence of dimers (molecules) in solutions of alkali metals in their molten halides has already been suggested to explain a minimum in the electrical conductance of these systems.[6]

It appears that the alkali metal can be present in three forms in the melt. In the case of dilute solutions (10^{-3} mole % metal) there is a possible interaction of the alkali metal with the melt to form an F-center. This configuration was suggested by Bredig[7] and can be inferred from the fact that the spectra of such dilute solutions are independent of the metal that has been added.[2] As the concentration of the metal is increased, the spectra can be interpreted in terms of the atomic and molecular species of the metal as has been done herein for the saturated solution of 675° C. Upon further increasing the metal concentration, the solution becomes optically opaque in the visible region typical of the metallic state. This result occured for the saturated solution of Na in NaI at a temperature of 700° C.

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(5) G. H. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Princeton, New Jersey, 1950.

(6) H. R. Bronstein and M. A. Bredig, Jr. Am. Chem. Soc. 80, 2077 (1958).

(7) M. Blander, "Molten Salt Chemistry," John Wiley & Sons., Inc., New York, 1964, p. 382.

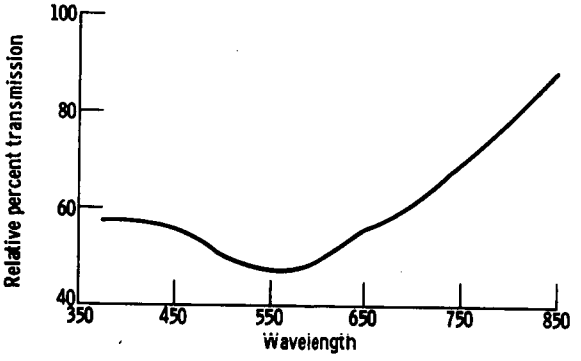

Fig. 1. - Visible absorption spectra of saturated solution of Na in NaI at 675° C.